

Quantitative Measurements of the Absorption of Light. I.—The Molecular Extinctions of the Saturated Aliphatic Ketones.

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The results of an examination of the absorption spectra of some saturated aliphatic ketones in alcoholic solution were published by Stewart and Baly,* and it was shown that there seemed to be a direct connection between the persistence of the absorption band and the chemical reactivity of the ketone in each case as measured by the rate of the formation of its oxime or sodium bisulphite compound. Since the date of that paper the technique of absorption methods has been considerably improved, and it appeared worth while to investigate the absorptive power of the same ketones with the more efficient methods now available.

It was found at once that there is a very considerable difference in the position of the absorption band according to whether the ketone is observed in the pure state or in solution. As is well known, the effect of the solvent generally is to shift the absorption maximum towards the longer wavelengths, this shift being as much as 100 Å.U. in the case of acetone and its aqueous solution. Moreover, it was also found that the shift varies irregularly from ketone to ketone, and it is therefore obvious that in order to compare the ketones amongst themselves it is necessary to deal with the pure ketones and not their solutions.

The only results that have been published of the absorptive power of the pure homogeneous ketones are those by Bielecki and Henri,† and by Purvis and McClelland.‡ In the first paper is given the absorptive power of pure acetone as determined by the well-known method of these authors, and, indeed, this is the only quantitative observation of the absorptive power of a pure saturated aliphatic ketone that has been published.

Purvis and McClelland state that in the case of diethyl ketone a layer 0·8 mm. thick with one minute exposure shows complete absorption of all the rays between $\lambda = 3050$ and $\lambda = 2420$, and of all the rays beyond $\lambda = 2280$. I find that with Kahlbaum's material once redistilled and a layer 0·5 mm.

* 'Trans. Chem. Soc.,' vol. 89, p. 489 (1906).

† 'Ber.,' vol. 46, p. 3627 (1913).

‡ 'Trans. Chem. Soc.,' vol. 101, p. 1810 (1912).

thick, the limits of absorption are $\lambda = 3050$, 2415, and 2290. These two results are in good agreement.

A general theory as regards the presence of absorption bands was put forward by Hartley, who postulated that they are due to molecular vibrations of a frequency comparable with that of light. This theory has been recently revived in a somewhat modified form by Hantzsch,* and by Henderson and Heilbron.† It is suggested that intramolecular vibrations take place, and that these give rise to electronic vibrations which form the origin of selective light absorption. If this theory were true it would be expected that the effect of substitution of the hydrogen atoms of acetone by alkyl groups would very considerably modify the absorptive power exerted. If the origin of the absorption is to be traced to the molecular vibrations, then surely great differences would be found between the absorptive power, for example, of acetone and pinacolone, or of acetone and methyl nonyl ketone.‡

On the other hand, from an extended investigation of the absorption spectra of certain groups of organic compounds, it has been shown that the molecular vibration theory is unsound, a conclusion that is strongly supported by the results published by Henri and his colleagues from their work upon the relation between the photochemical action of light on the ketones and their absorptive power. It has been shown that the origin of selective absorption of light by organic compounds would seem to be in the electromagnetic field surrounding the molecules, and that the light in being absorbed does work upon these fields and establishes a photodynamic equilibrium.§ Whereas the molecular vibration theory attributes the phenomenon of absorption to optical resonance, the electromagnetic force field theory attributes the absorption to the fact that the light does work upon the closed or partially closed electromagnetic fields. As has been previously shown, the latter theory affords an explanation of fluorescence and phosphorescence and at the same time establishes a direct relation between light absorption and chemical reactivity, which the molecular vibration theory entirely fails to do.¶

The application of the electromagnetic force field theory to the saturated aliphatic ketones enables certain deductions to be made as to the absorptive power of these compounds, and of these deductions every one has been confirmed by experiment. According to this view the origin of the absorption lies in the electromagnetic field surrounding the molecule as a whole.

* 'Ber.', vol. 43, p. 3049 (1910).

† 'Roy. Soc. Proc.,' A, vol. 89, p. 414 (1913).

‡ Baly and Rice, 'Trans. Chem. Soc.', vol. 101, p. 1475 (1912).

§ Baly, 'Phys. Zeit.', vol. 14, p. 893 (1913); 'Phil. Mag.', vol. 27, p. 632 (1914).

This field has its principal origin in the carbonyl group, and can only slightly be modified by the adjacent alkyl groups. Four important deductions at once follow as regards the absorption of these ketones.

Firstly, the substitution of hydrogen atoms near the carbonyl group by means of alkyl groups would only alter slightly the nature of the force field with the result that the wave-length of the light absorbed would slightly be altered.

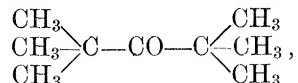
Secondly, a similar effect would be produced by dissolving the ketone in a solvent.

Thirdly, the substitution of a hydrogen atom by an alkyl group would have a smaller effect the farther removed the hydrogen atom is from the carbonyl group. The effect of substitution would be vanishingly small when the side chain of the ketone has reached a certain length.

Fourthly, the molecular absorptive power of all the ketones should be the same, that is to say, equal numbers of molecules of all the ketones should absorb the same quantity of light provided that the ketones are monomolecular and not associated.

As already stated, these deductions from the theory have all been experimentally confirmed.

When the present investigation was finished a second paper was published by Henderson and Heilbron, in which they suggested a method for putting their theory to a crucial test. In hexamethylacetone,



there are no hydrogen atoms immediately adjacent to the carbonyl group, and therefore this compound cannot undergo any change in chemical structure such as is postulated by these authors as the basis of absorption. This compound, according to their view, therefore should not show any selective absorption, and in their paper Henderson and Heilbron stated that they had examined this substance and found that it possessed no trace of selective absorption. According to the electromagnetic force field theory, it is obvious on the other hand that this compound should show selective absorption. Owing to the substitution of all the hydrogen atoms of acetone by methyl groups, the absorption band should only be altered in position, while the molecular absorptive power should be the same as that of all the other ketones.

Henderson and Heilbron do not give any details as to the preparation and purification of the hexamethylacetone as used by them, and owing to the essential importance of their observation it was thought advisable to repeat

their examination of this compound. A considerable quantity was therefore prepared and purified in the manner described below. It was then found to exhibit a strong absorption band in the expected position, and also to possess exactly the same molecular absorptive power as all the other ketones examined. This result makes Henderson and Heilbron's theory that the absorption is connected with a change in chemical configuration quite untenable, and seems in a very marked manner to confirm the view that the origin of the absorption lies in the electromagnetic field of the CO group as modified by the adjacent carbon and hydrogen atoms. The mechanism of absorption cannot be dynamic in the sense that the hydrogen atoms are labile.

On commencing this investigation, some preliminary observations showed that the ketones varied most irregularly amongst themselves as regards their absorptive power, and in this way, although the compounds had been fractionally distilled *in vacuo* with the greatest care and only the middle fraction used, doubt was thrown on their purity. It was further found that in treating the fractions with a dilute neutral solution of potassium permanganate an immediate reduction of the permanganate took place, thus proving that impurities were present. It was not found possible to purify any of the ketones by distillation alone, and chemical methods were employed in each case. It follows from this that all the results that have been published of the absorption by the ketones are vitiated by the fact that the ketones were not examined in a state of absolute purity, with the exception of Bielecki and Henri's measurement of acetone already referred to.

When by suitable means the pure ketones are prepared, a striking difference is at once noticed between the absorption curves before and after purification. The absorption curve, such as has been published by previous authors, is represented as having an absorption minimum on the ultra-violet side of the band, the absorption increasing on either side of this minimum. After purification this minimum disappears and the ketone becomes diactinic in this region. This is well shown in fig. 1, which gives the qualitative absorption curves of ethyl propyl ketone before and after purification.

It is obvious from this that the absorption minimum shown before purification is due to the presence of impurities, the general absorption of which is superposed upon the selective absorption of the pure ketone. An important point arises in connection with the presence of an impurity in the ketone. The absorptive power of these compounds is relatively very small compared with that of ring compounds. Consequently, the presence of such impurity, even in small amounts, would vitiate any quantitative measurement of the absorptive power of an aliphatic ketone. It is well known how readily

ketones, especially those containing the acetyl group, are converted into cyclic compounds, and therefore the rigid absence of such impurities is

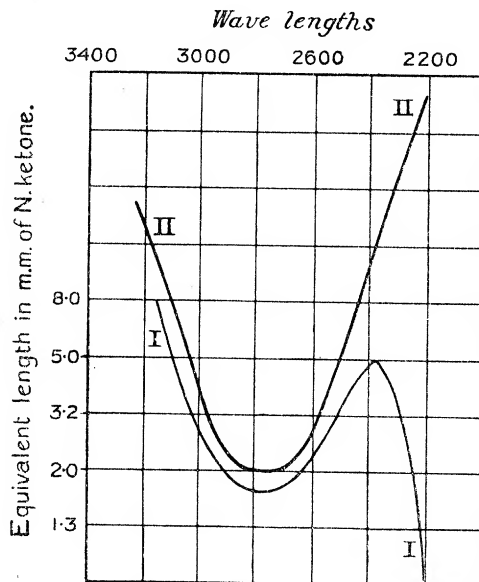


FIG. 1.—Ethyl propyl ketone.

I. Distilled *in vacuo*.

II. Purified through semicarbazone.

absolutely essential. It was evident therefore that before any reliable measurements of the ketones could be made it was absolutely necessary to prepare them in a state of purity.

The ketones used in this investigation were all purified with the greatest possible care, and no specimen was used for absorption measurements unless it showed itself to have no trace of an absorption minimum on the ultra-violet side of the absorption band, and to give no reduction of a dilute neutral solution of potassium permanganate when shaken with it for 15 minutes. When this was found to be the case the compound was considered to be optically pure.

The following methods were employed in the purification of the several ketones:—

Acetone.—Kahlbaum's material, prepared from the sodium bisulphite compound, was used after careful redistillation. The optical test mentioned above seemed to establish its purity, but in order to confirm this conclusion the acetone was treated according to the method described by Shipsey and Werner.* The absorptive power was not altered in the smallest degree by this treatment.

* 'Trans. Chem. Soc.,' vol. 103, p. 1255 (1913).

Methyl Ethyl Ketone, Methyl Propyl Ketone, Methyl iso-Propyl Ketone, Diethyl Ketone, Methyl Butyl Ketone, Methyl iso-Butyl Ketone, Methyl Hexyl Ketone, and Methyl Nonyl Ketone.—These ketones were all purified by conversion into the sodium bisulphite compound, from which the original ketone was regenerated. The ketone was shaken with an excess of a saturated solution of sodium bisulphite until the maximum possible yield of the addition compound had been formed. In the case of the higher ketones a little alcohol was added to increase the velocity of the combination. The mixture was filtered at 0° C. and the double compound thoroughly drained, washed once or twice with ether, and dried on a porous plate. The dried material was transferred to a flask containing a solution of sodium carbonate. The ketone was then, if possible, distilled off in a current of steam. With the higher boiling ketones this was found to be impossible, owing the formation of coloured impurities which could not be removed by any means. In these cases the steam was passed into the alkaline solution for just sufficient time to decompose the addition compound. The solution was then cooled and the ketone mechanically separated.

In the case of the lower boiling ketones which were distilled in a current of steam, the aqueous distillate was treated with potassium carbonate in order to salt out the ketone, which could then be mechanically separated. In every case the ketone was treated with a little alkali in order to remove any trace of sulphur dioxide or carbon dioxide.

The several ketones prepared in this way were dried for 48 hours over fused calcium chloride and then distilled. If the boiling point of the liquid were 100° or less, the distillation was carried out under ordinary pressure, but if the boiling points were above 100° the distillation was always carried out under reduced pressure.

Pinacoline.—This was purified by conversion into the oxime. This compound was prepared according to the method given by Lapworth and Steele.* The oxime, when thus obtained, was recrystallised from alcohol. It was then filtered and dried on a porous plate. The pure oxime was then transferred to a flask containing a 10-per-cent. aqueous solution of sulphuric acid and the pinacoline distilled over in a current of steam. A certain amount of undecomposed oxime was found to be carried over with the pinacoline. This was removed by shaking the ketone with a 15-per-cent. solution of sodium hydroxide, after which it was washed with water, dried, and distilled.

Ethyl Propyl Ketone, Dipropyl Ketone, and Ethyl iso-Butyl Ketone.—The first attempts to purify these compounds were made by means of their oximes,

* 'Trans. Chem. Soc.,' vol. 99, p. 1882 (1911).

but this was found to be impracticable owing to the fact that the oximes are oils which would not crystallise, even at very low temperatures. The final method adopted was to convert these ketones into their semicarbazones, from which the pure substances were regenerated. The method of procedure was exactly similar to that used in the case of the oximes and described above for pinacolone.

A further purification was made of dipropyl ketone by recrystallising it from hexane at a temperature of -80° . For this purpose a special apparatus was devised to enable the crystals to be filtered off at the low temperature. It was found, however, that the ketone, after the recrystallisation, had identically the same absorptive power.

Hexamethylacetone.—This compound was prepared from pinacolone according to the method described by Haller and Bauer.* From 100 gm. of pinacolone about 60 gm. of the crude ketone boiling at $159-161^{\circ}$ were obtained. Since this ketone does not form an oxime, semicarbazone, or hydrazone, the problem of its purification seemed to present some difficulty. A preliminary test showed that on shaking with potassium permanganate solution considerable reduction took place. The whole of the ketone was therefore shaken with successive portions of permanganate solution until no further reduction took place. The ketone was then washed with water, alkali, acid, and again with water. After drying the ketone was distilled with a Young fractionating column, and almost the whole quantity passed over at $161-161.5^{\circ}$. The absorption was then examined, and, as already mentioned, it was found to exert strong selective absorption and to possess the same molecular absorptive power as the other ketones.

In order to place its purity beyond question, the ketone was recrystallised from absolute methyl alcohol at -80° . The separated crystals, after melting, were washed with water, dried, and distilled under reduced pressure. The whole of it distilled at 61.5° at 15 mm. pressure. No change was made in the absorption by this treatment, and the purity of the ketone was thus established beyond any question.

The boiling points of the ketones are shown in the table on p. 83.

The preliminary part of this investigation was carried out with a large quartz spectrograph, the usual qualitative absorption curves being obtained. In order to obtain the requisite thin layers of the liquids, the micrometer cell as previously described was used.† This method of work was superseded by the spectrophotometric arrangement recently devised by the firm of Hilger and Co. With this apparatus it is possible to determine the extinc-

* 'Comptes Rendus,' vol. 150, p. 582 (1910).

† 'Baly and Rice,' 'Trans. Chem. Soc.,' vol. 103, p. 91 (1913).

Ketone.	Boiling point.	Pressure.
	°	mm.
Acetone	56·3	759
Methyl ethyl ketone	80·1	758
Methyl propyl ketone.....	101·5	759·2
Methyl isopropyl ketone	94·7	756·4
Methyl butyl ketone	125·5	758·3
Methyl isobutyl ketone	115·8	759·3
Pinacolone	106·2	759·3
Methyl hexyl ketone	169·5	758·9
Methyl hexyl ketone	65·2	12
Methyl nonyl ketone	99·1	12
Diethyl ketone	101·0	761·5
Ethyl propyl ketone	123·4	757·2
Dipropyl ketone	75·1	68
Hexamethylacetone	64·5	15
The melting point of pinacolone oxime was found to be 75·5°.		

tion coefficient to as far as 2100 Å.U. As a measure of the accuracy of this instrument it may be said that it has been found possible to find the position of maximum absorption, that is to say the optical centre of the absorption band, to within ± 3 Å.U.

The extinction coefficient, ϵ , is given by

$$\epsilon = \frac{1}{d} \log \frac{I_0}{I},$$

where I_0 is the intensity of the incident light, I the intensity of the emergent light, and d the thickness of the absorbing layer.

In order that the results be comparable it is necessary to take into account the molecular concentration of the ketone. If c be the normality of the ketone (Specific gravity \times 1000/Molecular weight), the molecular extinction is given by $M = \epsilon/c$.

The molecular extinction curves are obtained by plotting the values of M on the ordinates against the corresponding wave-lengths on the abscissæ. Owing to the compactness of the spectrophotometric apparatus it was not found possible to use the micrometer cell, but a number of cells were made of known thicknesses by cementing together two plain parallel quartz plates together with a wire ring of known diameter between them.

The thickness of the two quartz plates being known, it was possible to measure the distance between them to within 0·003 mm. Several cells were made to hold liquid layers from 0·8 mm. to 2·0 mm., and found to be sufficient for all the ketones examined.

The extinction curves may be discussed from two points of view, namely, the optical centres of the absorption bands, and the molecular extinctions

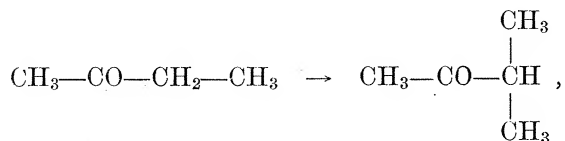
at the centres. The wave-lengths of the centres of the absorption bands are given in the following table:—

Table I.

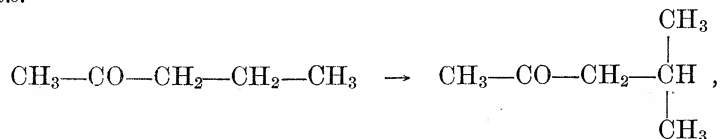
Acetone	2747	Methyl <i>isopropyl</i> ketone.....	2820
Methyl ethyl ketone	2770	Methyl <i>isobutyl</i> ketone	2810
Methyl propyl ketone.....	2790	Pinacolone	2850
Methyl butyl ketone	2790	Diethyl ketone	2780
Methyl hexyl ketone	2790	Ethyl propyl ketone	2800
Methyl nonyl ketone	2790	Dipropyl ketone	2820
		Ethyl <i>isobutyl</i> ketone	2820
		Hexamethylacetone.....	2950

The effect of substitution of the hydrogen atoms by CH_3 groups is shown in a very interesting manner in the above table. In the first column are given the values for the normal ketones containing the acetyl group, and as may be seen the substitution of an α -hydrogen atom in acetone to give methyl ethyl ketone, *i.e.* $\text{CH}_3\text{—CO—CH}_3 \rightarrow \text{CH}_3\text{—CO—CH}_2\text{—CH}_3$, causes a shift to the red of 23 Å.U. The substitution of a β -hydrogen atom in the latter, *i.e.* $\text{CH}_3\text{—CO—CH}_2\text{—CH}_3 \rightarrow \text{CH}_3\text{—CO—CH}_2\text{—CH}_2\text{—CH}_3$, causes a further shift of 20 Å.U. Substitution of a γ -hydrogen atom makes no difference, and thus in methyl propyl ketone the limiting length of side chain has been reached. The general conclusion may be drawn, therefore, that all normal ketones having the formula $\text{CH}_3\text{—CO—CH}_2\text{—CH}_2\text{—R}$, where R is any saturated alkyl radical, have absorption bands with centre at $\lambda = 2790$ Å.U.

The substitution of a second α -hydrogen atom by CH_3 , *i.e.*

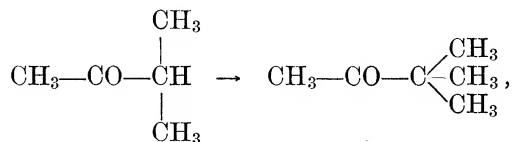


methyl *isopropyl* ketone, causes a shift of 50 Å.U., a much greater effect than that observed in the first substitution. This is doubtless due to the formation of the *iso* group, which will be referred to below. This exaltation due to the *iso* group is not evidenced when it is in the β -position for the substitution in methyl propyl ketone to give methyl *isobutyl* ketone, *i.e.*



only gives the normal shift of 20 Å.U.

The substitution of the third α -hydrogen atom in methyl isopropyl ketone to give pinacolone, *i.e.*



causes a further shift of 30 Å.U.

The shifts obtained in the successive substitution of the three α -hydrogen atoms of acetone are 23, 50, and 30 Å.U. respectively.

The last five ketones show the effect of substitution on *both* sides of the carbonyl group, and, as may be seen, the same laws are obeyed, namely, that substitution in the α - and β -positions only causes a shift in the centre of the absorption band. The case of hexamethylacetone is peculiarly interesting. The substitution of the three α -hydrogen atoms in acetone by methyl to give pinacolone causes a shift of 103 Å.U., and therefore it is to be expected that the substitution of all six α -hydrogen atoms should cause a shift of twice this amount, *i.e.* 206 Å.U. The centre of the absorption band of hexamethylacetone should be at $2747 + 206 = 2953$ Å.U. The observed value is 2950.

Turning now to the molecular extinction curves of the ketones, it may be pointed out that the curves of the ketones of the general formula $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_2-\text{R}$, where R is any saturated alkyl radical, are all absolutely identical. Further than this, the extinction curves of all the remaining ketones, with the exception of acetone and methyl ethyl ketone, are geometrically similar. It is possible, therefore, to draw one general curve from which the molecular extinctions at any wave-length may be found for any ketone, excepting the two just mentioned.

The following table gives the wave-lengths and molecular extinctions for the ketones of the general formula $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_2-\text{R}$:—

Table II.

Molecular extinction.	Wave-lengths.	Molecular extinction.	Wave-lengths.
5	3220 2416	15	2973 2605
7	3080 2471	17	2949 2631
9	3050 2510	19	2920 2660
11	3024 2544	21	2844 2636
13	2996 2576	21.2	2790

The maximum molecular extinction for all these ketones at the centre of the absorption band is therefore 21.2. These values are plotted on a curve in fig. 2, the figures on the curve being the last two significant

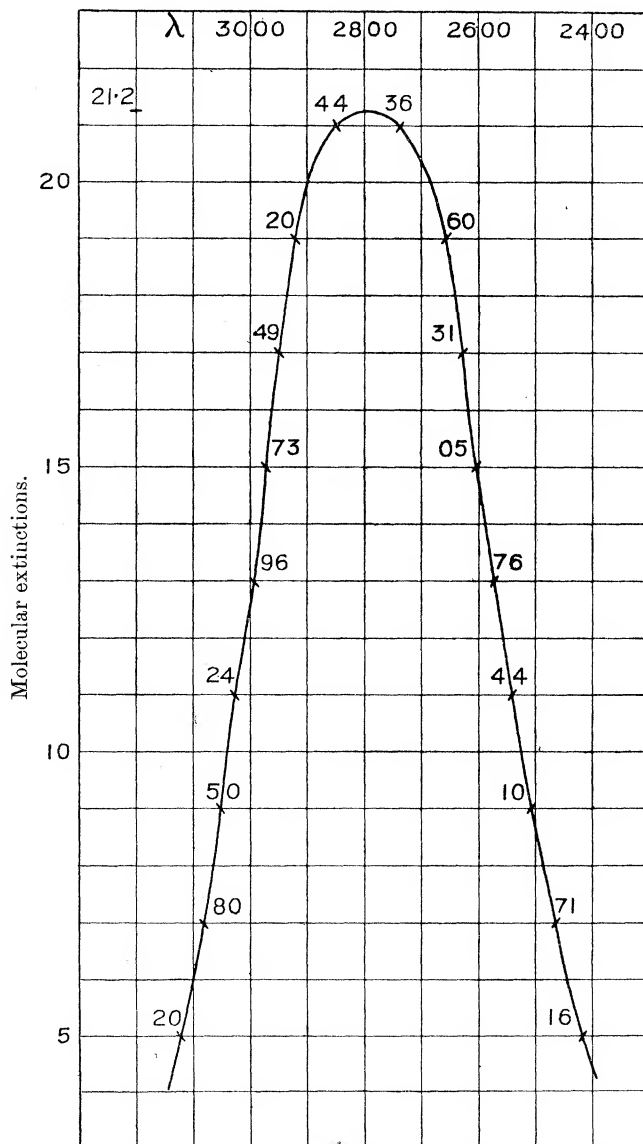


FIG. 2.—Curves for the ketones of the general formula $\text{CH}_3\text{—CO—CH}_2\text{—CH}_2\text{—R}$.

figures of the wave-lengths corresponding to the extinction shown on the ordinates. Owing to the geometric similarity, the molecular extinction curve of any ketone in the right-hand column in Table I may be drawn by adding

the difference between the centre of its absorption band and 2790 to the wave-lengths in Table II. It may be mentioned here that in the case of ketones with very long side chains the absorption of the alkyl radicals will be superimposed on the normal curve, but with all the ketones examined the absorption of the side chains was found to be practically negligible at wave-lengths greater than 2300.

Two important facts may be mentioned in connection with the results of these observations. In the first place, the measurements of the magnetic rotation carried out by Sir W. H. Perkin should bear some relation to the absorption observations, since there is no doubt that the electromagnetic force field theory also can offer an explanation of the magnetic rotation phenomena. A comparison of Perkin's results with the ketones, and those recorded above, certainly shows considerable analogy. For example, Perkin showed that in any one homologous series of compounds it is possible to lay down certain definite laws as regards the relation between magnetic rotation and constitution. Thus he found that the substitution of hydrogen atoms by methyl groups gave rise to a constant change in the molecular rotation, provided that the substitution did not take place in close proximity to a group possessing strongly marked residual affinity. As a result of this he was able to calculate the "series constant" of any homologous series, and in the case of ketones of high molecular weight perfectly accurate values were obtained.

On the other hand, considerable divergences showed themselves in the case of the ketones of low molecular weight. There certainly seems, therefore, some analogy between the light absorption values and those from magnetic rotation if we compare the two divergences together.

Thus the progressive substitution of methyl for hydrogen near the carbonyl group affects the extinction curves, the normal curve not being obtained until the γ -hydrogen atoms are reached.

A still more striking analogy is evidenced when the results with methyl isopropyl ketone and pinacolone are compared. Deviations are observed in the two cases of absorption and rotation. This is especially emphasised in dealing with methyl isopropyl ketone in which the *iso* group considerably increases the wave-length of the centre of the absorption band. Perkin showed that the presence of this grouping also abnormally increased the magnetic rotation.

A second striking fact is to be found in the chemical reactivity of the ketones, especially of the hydrogen atoms as regards their substitution by halogen atoms. It is well known that the direct substitution of the terminal hydrogen atoms in propane by halogen atoms is slow and difficult to bring

about, whilst in acetone the substitution is carried out with extreme ease. From the absorption results it is obvious that there is a very intimate connection between the carbonyl group and these hydrogen atoms, for substituting them by methyl causes a marked shift in the absorption band. This change is less if a β -hydrogen atom is substituted, and vanishingly small if a γ -hydrogen atom is substituted. In other words, the relation between

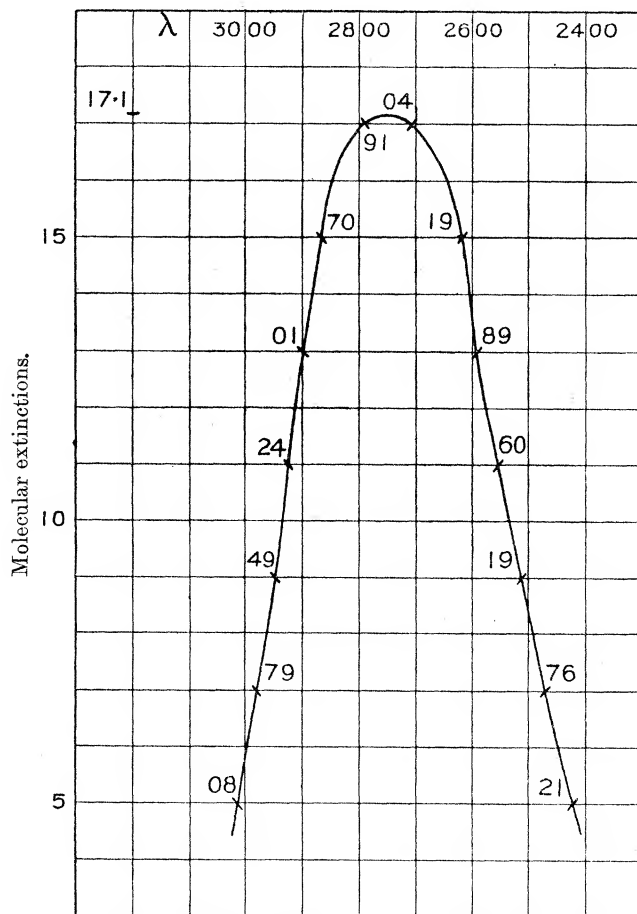


FIG. 3.—Acetone.

the carbonyl group and the α , β , and γ -hydrogen atoms decreases. The reactivity of the hydrogen atoms as evidenced by their direct replacement by halogen, must, therefore, decrease the further they are removed from the carbonyl group, the three γ -hydrogens of methyl propyl ketone being in exactly the same state as the terminal hydrogens of *n*-pentane.

Attention has already been drawn to the fact that the molecular extinc-

tions of acetone and methyl ethyl ketone are not the same as that of all the other ketones. The extinction curves of these two substances are shown in figs. 3 and 4, from which it can be seen that the molecular extinction of acetone is 17.1, and that of methyl ethyl ketone 19.4. These bodies, there-

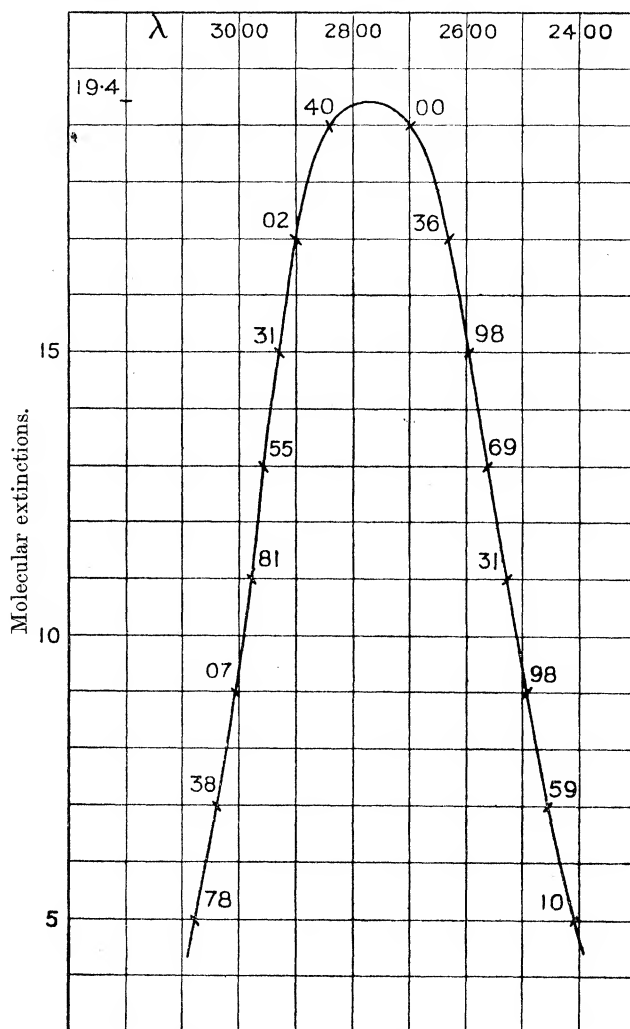


FIG. 4.—Methyl ethyl ketone.

fore, absorb less light than the other ketones, all of which have a molecular extinction of 21.2. This variation seems to be of considerable importance in view of the fact that acetone is known not to be entirely monomolecular but associated to a certain extent. Ramsay and Shields* found the factor of

* 'Trans. Chem. Soc.,' vol. 63, p. 1059 (1893).

association to be 1.26, that is to say, the average molecular weight of acetone is 58×1.26 . Now the association factor x is given by

$$x = \frac{N}{M_s + M_c},$$

where N is the total number of acetone molecules, M_s the number of simple molecules, and M_c the number of complex molecules. It is obvious that any association must tend to decrease the absorptive power of the ketone, and it is a reasonable assumption to make that the absorptive power of the associated molecule will be inversely proportional to the number of simple molecules in the complex, that is to say, if two molecules associate, the complex will absorb half as much as the two simple molecules, and so on. Obviously the calculated molecular extinction, in the case of acetone 21.2, will be proportional to N , assuming, of course, that if acetone were unassociated it would behave as a normal ketone in which the maximum molecular extinction is 21.2.

Again, the observed molecular extinction will be proportional to $M_s + M_c$, for this extinction is the sum of the absorptions of the associated and unassociated molecules for the particular wave-length.

We can, therefore, put the association factor $x = \text{Calculated molecular extinction} \div \text{Observed molecular extinction}$.

In the case of acetone $x = 21.2/17.1 = 1.24$, which is remarkably close to that actually observed by Ramsay and Shields, namely 1.26.

It would follow from this that not only is it possible to explain the divergency of the absorptive power of acetone from the normal value on the grounds of its association, but also actually to measure the association factor by means of the amount of light absorbed. To calculate the association factor, therefore, the ratio of the two extinctions (calculated and observed) is found. In the case of methyl ethyl ketone the observed value of the molecular extinction is 19.4, while the calculated value is 21.2. The ratio $21.2/19.4 = 1.09$ gives the association factor. Unfortunately no values of the surface tension of this ketone seem to have been published from which the value $d[\gamma(MV)^{2/3}] / dT$ may be calculated, but my results would certainly show that it is associated to this extent.

Summary and Conclusions.

1. Fourteen saturated ketones of the aliphatic series have been prepared in a state of optical purity.
2. Spectroscopic and chemical tests prove that their purity is above question, and that the absorptive power as determined for these ketones is thoroughly reliable.

3. The wave-lengths of the centres of the absorption bands depend on the number of methyl groups in the α and β positions relative to the carbonyl group. Substitution of hydrogen atoms in the γ or further positions has no effect on the absorption band.

4. The ketones of the general formula $\text{CH}_3\text{COCH}_2\text{CH}_2\text{R}$ have the centre of the absorption band at 2790, and those of the general formula $\text{RCH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{R}$ at 2820, where R is any saturated alkyl radical.

5. Substitution of an α -hydrogen atom by methyl causes a movement of the centre of absorption 20 Å.U. to the red for each atom substituted. Substitution for an α -hydrogen atom with formation of the *iso* group causes a shift of 50 units, and when the substitution in the α -position forms a tertiary group the centre of absorption moves 30 units. There is thus an enhanced effect in the case of the *iso* and *tert* groups. The movement of the band caused by the substitution of hydrogen by alkyl is always towards the red end of the spectrum.

6. The general results agree markedly with the observations made by Perkin on the magnetic rotation of these compounds. The magnetic rotation is normal for methyl propyl ketone and the higher homologues, but abnormal in the case of methyl ethyl ketone, and still more abnormal in the case of acetone. This is shown by the different position of the absorption bands in the case of acetone and methyl ethyl ketone from those of methyl propyl ketone and the higher homologues. A similar agreement between absorption and magnetic rotation is observed in the effect of the *iso* grouping.

7. The results of the absorption measurements agree with the chemical properties of the ketones. The former show that the farther removed from the carbonyl group is a hydrogen atom, the less effect is produced on substitution by methyl, or the less is the relation between the hydrogen atom and the carbonyl group. This is in agreement with the behaviour of the hydrogen atoms on treating the ketones with chlorine or bromine.

8. The absorptive power or molecular extinction of all the ketones, with the exception of acetone and methyl ethyl ketone, is 21.2. On the assumption that if acetone were unassociated it would behave normally, the association factor is calculated from its molecular extinction to be 1.24. This number is remarkably close to that found by Ramsay and Shields, namely 1.26.

Similarly, the association factor of methyl ethyl ketone is calculated to be 1.09. The method of light absorption measurement appears to give a means of determining the association factor of a liquid, and also it is not subject to any possible error due to surface concentration phenomena. Ramsay and Shields' work has been criticised on these grounds.

9. The whole of the measurements given are in agreement with the general theory that the absorption band of the ketones is due to the electromagnetic field of the carbonyl group as influenced by the substituents in the immediate neighbourhood.

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Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin.—II.

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§ 1. *Introduction.*

This paper is in continuation of a former one.*

It has been observed by Stark,† and subsequently by Matthies‡ and Child,|| that a luminous jet of mercury vapour, distilling away from the arc *in vacuo*, into a region quite remote from the electric field of the arc itself, may be deprived of its luminosity by an independent electric field.

The present paper describes experiments made to elucidate this effect in the case of mercury, and similar observations made upon other metallic vapours.

§ 2. *Experiments with Mercury. Electrical Condition in the Luminous Jet.*

Fig. 1 shows a form of apparatus suitable for many of the experiments. The mercury cathode is formed by the top of a barometric column, *a*, connected at the bottom to a rubber tube and reservoir (not shown). The hollow iron tube *b*, 5 mm. internal diameter and about 1 cm. long, forms the anode. It does not touch the glass walls, but is supported on an iron

* 'Roy. Soc. Proc.' A, vol. 90, p. 364 (1914).

† 'Ann. d. Phys.,' vol. 14, p. 530 (1904).

‡ 'Verh. d. Deut. Phys. Gesell.,' vol. 12, p. 754 (1910).

|| 'Phil. Mag.,' vol. 26, p. 906 (1913).